

AQUEOUS PHOTOLYSIS OF METHYLGLYOXAL AND ITS PRODUCTION OF
CARBOXYLIC ACIDS

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ABSTRACT

Highly soluble in water and absorbing in the lower tropospheric solar spectrum, methylglyoxal (MG), produced from oxidation of atmospheric hydrocarbons, is readily scavenged into hydrometeors and may undergo aqueous photolysis to produce downstream products such as carboxylic acids. Using a photochemical reactor equipped with a Hg lamp shielded by a Pyrex sleeve, we determined the products of MG photolysis as a function of pH and added trace components. At initial $[MG] = 10 \mu M$ and $pH = 3$, formic and acetic acids were produced in equimolar concentrations at a yield of unity. Hydrogen peroxide, peracetic acid and pyruvic acid were not detected. The reaction rate and stoichiometry are essentially independent of pH between 2 and neutral. The presence of $5 \mu M HNO_2$ resulted in the formation of pyruvic acid at a ~25% yield; the addition of $6 \mu M H_2O_2$ had no effect. These observations are consistent with homolytic fission of MG followed by reaction with H_2O , in which neither OH nor HO_2 is a major chain carrier. The rate of photolysis in sunlight (summer noon, $42^\circ N$) was $12 \% hr^{-1}$, marginally important for removing ambient MG. However, the in-cloud formation of formic and acetic acids from MG photolysis, $\sim 0.03 \text{ ppb } hr^{-1}$, (at $[MG] = 0.1 \text{ ppb}$ and $LWC = 1 \text{ g m}^{-3}$), contributes negligibly to these carboxylic acids.